

**QUANTITATIVE ANALYSIS OF COAL AND COAL COMPONENTS BY
SCANNING ELECTRON MICROSCOPY AND ELECTRON MICROPROBE ANALYSIS**

By

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Introduction

Quantitative compositional data for coal typically consists of bulk chemical data for organic elements and analyses of the inorganic elements in ash. This paper focusses on bringing together procedures primarily using scanning electron microscopy (SEM) and electron microprobe analysis (EMPA) to obtain:

- (1) The inorganic element content of bulk coal samples.
- (2) The inorganic element content of specific lithotypes and macerals in coal.
- (3) The abundance of macerals in coal (using standard petrographic techniques).
- (4) The inorganic element content of specific mineral phases in coal.
- (5) The abundance of mineral phases in coal.

SEM/EMPA techniques allow both inorganic analysis of bulk materials and determination of chemistry and abundance of microscopic constituents. This approach provides data on individual components which may be significant in assessing

the origin of a specific coal, its diagenetic and weathering history, and its behavior during utilization.

This paper summarizes a series of procedures which are combined to provide a more complete method of quantitative analysis of coal. Examples are presented that illustrate results of the use of these various procedures in understanding coal origin and utilization.

Methods

Methods summarized in this paper have been developed at the UND Energy Research Center and Department of Geology and Geological Engineering for a variety of applied coal science studies at the Center and academic research and thesis projects at the Department.

Sample Preparation: Sample preparation for analysis of bulk coal by EMPA has been described by Karner and others (1986). Samples were ground to a fine powder, vacuum-dried and compressed under 10 tons pressure to form two flat pellets for each standard and unknown coal. Samples for analysis of minerals in coal have been described by Kleesattel (1985) and Zygarlicke (In Preparation). Vacuum dried samples of low-rank coal were crushed by mortar and pestle to pass a 20 mesh screen. The coal was mixed with epoxy and pressed into cylindrical molds 25 mm in diameter. Vacuum impregnation and/or pressing was used to eliminate air bubbles. After hardening, the epoxy plugs were cut and polished using procedures dependent upon the materials studied. For mineral analysis and abundance determinations, standard procedures using water and oil as fluid media for sawing and grinding were followed (Zygarlicke, In Preparation). For

maceral abundance using light microscopy, standard ASTM techniques were utilized (Kleesattel, 1985). For analysis of inorganic elements in macerals, a series of procedures are being evaluated. Preliminary results show that water should not be used and that grinding and polishing dry or with minimal use of oil is best when Na and other easily removed elements are present. All samples for EMPA were carbon-coated.

Analysis of Bulk Composition by EMPA: A quantitative method for the analysis of the inorganic elements in bulk coal samples is given in Karner and others (1986). A peak-to-continuum (P/C) ratio method is used instead of standard ZAF correction procedures because of the heterogeneous character, low density, and light element composition of coal and other organic materials. Similar procedures have been developed by workers in the biological sciences (Hall, 1968; Russ, 1974; Statham and Pauley, 1978 and Small and others, 1980).

In the P/C method, as an initial approximation, continuum and characteristic radiation are similarly affected by changes in particle size, density and specimen thickness. The ratio of peak intensity; to continuum intensity is approximately constant for a given elemental concentration. A study of nine National Bureau of Standards (NBS) reference standards including four bituminous coals, two subbituminous coals and three dried plant materials was used to evaluate the P/C method (Karner and others, 1986). Operating conditions of a JEOL 35C microprobe system were 15 keV accelerating voltage and 920 picoamperes beam current. The probed area was approximately one square millimeter and the analysis time 400 seconds. A Kevex, lithium-drifted silicon, solid state detector was used with a Tracor-Northern TN2000 x-ray analysis system. The region 2.00

- 5.00 keV was used for measurement of continuum intensity. A reference library of pure element and oxide standard spectra was used with the Tracor-Northern XML least squares fitting routine to generate peak-to-continuum elemental ratios.

Analysis of the standards provided data to calculate the elemental composition of unknowns as well as a means of testing linearity of the plots of determined and expected concentrations for the standards. It was concluded (Karner and others, 1986) that the method performed well for Al, Ca, S and K; that a greater range of composition of standards was necessary to confirm the apparent good fit of Na, Mg, Si, P, Cl and Ti; and that Fe showed considerable scatter. More complete documentation of current standards and additional standards are necessary to improve results for the latter elements.

Analysis of Lithotype and Maceral Composition by EMPA: Early approaches to analysis of macerals by EMPA focussed on organic sulfur, for example studies by Sutherland (1975), Boenteng and Phillips (1976), Harris and others, (1977), Raymond and Gooley (1978) and Markuzewski and others (1981). Recent work is much more diverse and will not be surveyed in this paper. Our quantitative studies are based on the P/C approach outlined above and documented more completely in Karner and others (1986). The analytical procedure for lithotypes and macerals was identical to that for bulk coal except that smaller areas, typically from 20 to 70 square microns were used for analysis. Smaller areas and point analyses may result in observable beam damage to the specimen and larger areas typically are not homogeneous. Specific lithotypes are hand-picked and crushed into chips for analysis. Macerals were identified optically by examining

polished sections with a conventional reflected light microscope. However, macerals, particularly ulminite and vitrinite, were often easily recognized by their characteristic SEM secondary and/or backscattered electron images.

In order to obtain quantitative chemical data for lithotypes and macerals in sections of polished chips we have compared analyses of nearly homogenous materials prepared by two different methods as described above. Vitrain from the Hagel Bed at the Baukol-Noonan Mine near Center, N.D. was obtained from a single piece of fossilized wood about 10 cm in diameter. Megascopically, the vitrain was uncontaminated by extraneous material and came from a small zone in the wood. Part of the material was ground and analyzed as a sample of bulk coal and part was broken into chips and analyzed as the lithotype vitrain consisted essentially of the maceral ulminite. The results comparing bulk analysis and maceral analysis (Table 1) show that:

- (1) Average chemical compositions by both methods were very similar particularly for Na, Mg, S, K, Ca and Fe. This observation supports the validity of the use of the technique for epoxy-mounted chips.
- (2) Al, Si and Ti averaged 1.5 to 2.6 times as abundant in the powders as the vitrain chips showing that additional aluminosilicate mineral material was incorporated in the powders but was not present in the clear unfractured and unaltered areas of the chips which were selected for analysis. These observed variations suggest that further analysis of the distribution of aluminosilicate material in vitrain should be undertaken. Synthetic, homogeneous material of appropriate chemistry

should be sought to further test the relationship between analyses of powders and chips.

Analysis of Abundance of Macerals: Standard procedures of coal petrography modified for low-rank coals as described by Kleesattel (1985) must be used to determine the abundance of maceral types in low-rank coals.

Analysis of Mineral Phases by EMPA: Conventional microprobe techniques may be used in the study of minerals in coal. In practice, the same epoxy plugs used to analyze macerals are examined for mineral grains using secondary and back-scattered images. Size, shape, chemistry and association with other minerals and with macerals may be determined. Chemistry is determined using the previously described analytical procedures with matrix correction by conventional ZAF or Bence-Albee procedures.

Analysis of Abundance of Minerals: Standard methods of point counting adapted to the characteristics of the SEM/EMPA systems, and to the distribution of minerals in coal fragments were used. The automated stage of the SEM system was programmed to move the epoxy plug in increments of equal length under the stationary electron beam. A grid of analysis points was established so that 500 points on macerals and minerals were obtained over an area of 2.0 - 2.5 cm². Points on epoxy ranged up to 30 percent of those on macerals and minerals but were disregarded. An elemental energy spectrum was obtained at each point and used to distinguish between macerals, minerals, and epoxy. Data was recorded on a manual counter. Mineral spectra were acquired over a period of 50 seconds and stored on a floppy disk for detailed examination. Mineral spectra were

recorded separately as specific phases and all maceral spectra were recorded as coal. Low rank coals typically contained 3-4 minerals of major abundance and rarely had more than 10 different minerals. Many minerals had spectral patterns which were easily recognized. Clay minerals were most difficult to identify. Percentages of total oxides present were calculated by correction programs. Notable exceptions were H_2O and CO_2 affecting most strongly the analyses of clay minerals and carbonates. Combinations of maceral and mineral spectra were allotted to minerals if the oxide content exceeded 30 percent.

Application

The procedures described in this paper will enable a major advance in the analysis of coal and coal components, particularly in low-rank coals which contain relatively large amounts of inorganic elements which are organically bound. We have conducted several studies utilizing the recommended methods separately and are combining them in current studies. Two examples of the initial studies are summarized below.

Analysis of Macerals in Low-Rank Coals: The inorganic chemistry of huminite group macerals in four low-rank coals was summarized in Karner and others (1985a, 1985b, 1986). Analyses of ulminite representative of the Beulah-Zap (BZ) and Hagel (HG) lignites, ND, the Martin Lake (ML) lignite, TX, and vitrinite of the Rosebud (RB) subbituminous coal, MT were made using the P/C method (Karner and others, 1986). The results showed that the major huminite group maceral, ulminite or vitrinite, within a specific low-rank coal, has a relatively

high content of inorganic elements. The maceral composition within a coal has a limited range of variability and is distinct from that of other coals. A comparison of the four coals is discussed by Karner and others (1986). BZ ulminites have high Na and Fe and low S and total constituents, HG ulminites have high Ca and low Na and S, ML ulminites have low Na and high Mg, S and total constituents while RB vitrinite has moderate to low values for all elements. Within the coals, BZ and HG ulminites tend to occur as either low or high Na+Mg+Ca types, ML ulminite occurs as a low or high Al+Si type and RB vitrinite types vary from low to high Mg/Al ratio. The chemistry of the huminite group macerals and the bulk compositions of the four coals have striking similarities which are illustrated in Figure 1 (Karner and others, 1985b). BZ is a high Na and low S coal and its ulminite compositions plot relatively high in Na and relatively low in S compared to the other coals. Similarly, HG ulminite has low Na and high Ca and ML ulminite has low Na and high S matching the compositions of the respective coals. The P/C method provides a means to compare and relate the inorganic chemistry of whole coal and macerals. Such geochemical characterization may have great significance for the development of our understanding of coal formation and coal utilization.

Abundance of Minerals in the Harmon Lignite Bed: The SEM/EPMA mineralogy of the Harmon lignite bed from the Gascoyne Mine, ND has been determined by point-count methods by Zygarlicke (In Preparation). Ash, mineralogy and combustion data are given in Table 2. Sodium is the major factor determining fouling in North Dakota lignites. The White Pit and Blue Pit coals have different combustion behaviors and variable sodium contents. Sodium content is not an adequate guide for combustion behavior in this case. Normally one would expect the Blue

pit coal to have the strongest fouling tendency because of its higher sodium content, however, the White pit coal is much more severe in its fouling tendency. The severe fouling of the White Pit coal is thought to be a direct result of the high clay mineral and quartz contents of the coal. The Blue Pit coal which was less severe in its behavior had lower clay mineral and quartz contents. These observations may indicate that the greater availability of aluminosilicate material in the White pit coal allowed for the formation of much harder and more extensive ash fouling deposits. Quantitative information on the abundance of mineral phases is useful in interpreting behavior of coal during utilization.

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Table 1. Results of Microprobe Analyses Comparing Weight Percentages of Elements Determined in Ground Samples Versus Epoxy-mounted Chips of Vitrain

<u>ELEMENTS</u>	<u>AVERAGE FOR FOUR AREAS OF GROUND POWDER PELLET</u>	<u>AVERAGE FOR SINGLE AREAS ON EACH OF FIVE GRAINS</u>
Na	0.34	0.39
Mg	0.30	0.26
Al	0.74	0.28
Si	0.14	0.09
S	1.28	1.42
K	0.03	0.03
Ca	1.18	1.16
Ti	0.05	0.02
Fe	0.07	0.07

Table 2. Ash, Mineral and Combustion Data for Gascoyne Mine Lignite

	<u>White Pit</u>	<u>Blue Pit</u>	<u>Red Pit</u>
Quartz	10.06	3.34	2.35
Kaolinite	1.12	0.39	0.39
Montmorillonite	0.70		
Pyrite	1.41	2.23	2.23
Illite	0.77		
Unknown Clay Mineral		0.39	
Gypsum			1.04
Hematite		0.78	
Chlorite			0.44
Total Minerals*	14.07	7.14	6.45
Ash*	17.10	10.12	10.30
Na ₂ O**	3.50	6.90	2.70
Fouling Tendency	Severe	High	Medium

*Weight percent of coal

**Weight percent of ash

FIGURES

Figure 1. S-Na-Ca Plot of Characteristic Ulminite Types in Beulah-Zap and Hagel Lignites, North Dakota, Martin Lake Lignite, Texas and Vitrinite in the Rosebud Subbituminous Coal Montana.

